Novel Chiral Di-2-pyridyl Ketone Ligands: Crystal Structure of a Copper Complex and its Activity in the Copper-Catalyzed Enantioselective Cyclopropanation of Styrene

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Keywords: Chiral auxiliaries / Asymmetric catalysis / Pyridyl / Nitrogen heterocycles / Cyclopropanation / Copper

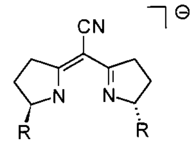
New C_2-symmetric chiral di-2-pyridyl ketones were prepared from readily available chiral bromopyridines. Their complexes with copper were synthesized and characterized by X-ray crystallography. The copper complexes were prepared in situ with the triflate anion and were found to be active in the catalysis of cyclopropanation with diazo esters and alkenes. Reaction yields were excellent and enantioselectivities of up to 61% were observed.

Introduction

The synthesis of chiral ligands has been of crucial importance in the development of transition metal-catalyzed enantioselective reactions.[1] Chiral *N*,*N*-bidentate ligands such as semicorrine **1** and bis-oxazoline **2** have been found to be highly effective chiral controllers in asymmetric reactions.[2−4] We are particularly interested in chiral 2,2′-bipyridines **3**, which are structurally similar to these ligands and have also been employed in asymmetric catalysis.[5−11] Our strategy has been to synthesize new chiral ligands based on chiral pyridine.[12] Although di-2-pyridyl ketone and its hydrated form are structurally similar to 2,2′-bipyridine and are known to form complexes with various metal ions,[13] to the best of our knowledge there have been no reports of the synthesis of chiral di-2-pyridyl ketone ligands or their use in asymmetric catalysis. Herein, we report the synthesis of the new chiral di-2-pyridyl ketone ligands **4** based on readily available chiral bromopyridines, and the preparation and crystal structure of a copper(II) complex. We also report the study of the catalytic activities of the copper complexes in asymmetric cyclopropanation.[14]

Results and Discussion

The synthesis of the chiral di-2-pyridyl ketone ligands **4a−d** is summarized in Scheme 1. The enantiomerically pure starting materials, the 2-bromopyridines **5** and **6**, could easily be prepared from commercially available 2,6-dibromopyridine.[6a][6b] Compounds **4a−b** were obtained by the reaction of lithiated **5** and **6** with ethyl chloroformate,



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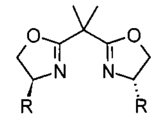

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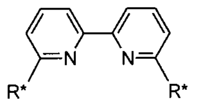

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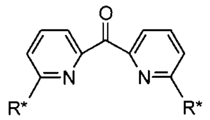

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while **4c−d** were prepared by using ethyl picolinate. The yields of **4a** and **4b** were both 65%, while those of **4c** and **4d** were 31 and 25%, respectively. The IR spectra of **4a−d** (KBr) show ν(C=O) in the range 1681−1687 cm^{-1}.

In order to investigate the coordination chemistry of these di-pyridyl ligands, the copper complex **7** was synthesized. It was obtained as a blue solid in good yield by mixing copper(II) perchlorate and **4a** in methanol and stirring overnight (Scheme 2). Crystals suitable for X-ray crystallography were obtained by recrystallization from acetonitrile/ether. The IR spectrum (KBr) shows ν(C=O) at 1687 cm^{-1}, which is identical to that of the free ligand. The X-ray crystal structure, shown in Figure 1, shows a 1:1 complex between Cu^{II} and the ligand. Table 1 summarizes the structural parameters of **7**. Ligand **4a** acts as a tetradentate ligand and the coordination geometry can be described as square pyramidal with the metal ion surrounded by two pyridine nitrogen atoms, two neutral oxygen atoms of the ether groups and one oxygen atom from one of the perchlorate anions. The perchlorate anion interacts with the copper(II) ion and occupies the apical position. Because of this interaction, the C_2 symmetry of the ligand is slightly distorted. The planar pyridine rings are twisted differently

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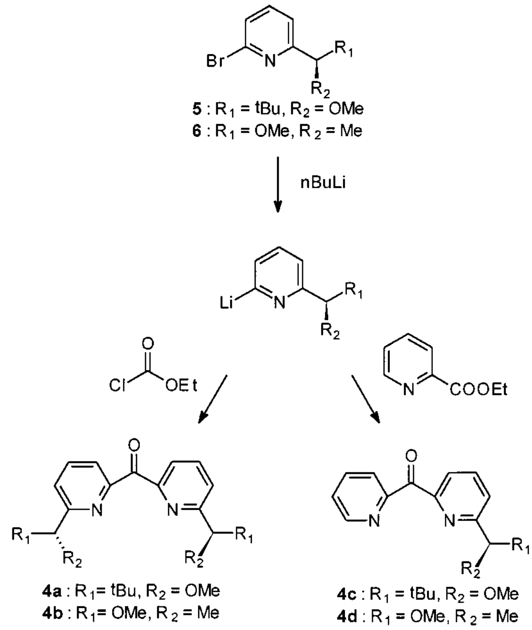
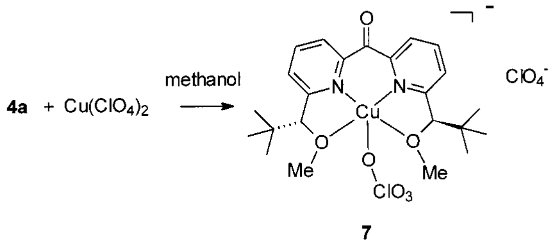


Scheme 1. Synthesis of chiral di-2-pyridyl ketone ligands

around the planar ketone subunit C7−C(O)−C9 by torsional angles of 6.17° and 21.68°, and the planes of the two rings are twisted by 24.47° relative to each other. The copper−nitrogen bond lengths are 1.960 and 1.944 Å, which are slightly shorter than those of other achiral pyridyl ketone complexes.[13b][13f] They are also shorter than a related chiral dichloro(bipyridine)copper(II) complex reported previously,[11b] where the Cu−N bond lengths are both 2.017 Å. The bite angle of 96.3° made by the chiral dipyridyl ketone and copper is much larger than that observed for the chiral bipyridine complex (83°).[11b] The copper−oxygen bond lengths are 1.987 and 2.006 Å.



Scheme 2. Synthesis of complex **7**

Table 1. Structural parameters for **7**

Atoms	Bond Lengths (Å)
Cu(1)−O(1)	2.006(4)
Cu(1)−O(3)	1.987(5)
Cu(1)−O(9)	2.261(6)
Cu(1)−N(1)	1.960(7)
Cu(1)−N(2)	1.944(6)
O(2)−C(8)	1.196(9)
	Bond Angles (°)
O(1)−Cu(1)−O(3)	95.5(2)
O(1)−Cu(1)−O(9)	89.3(2)
O(1)−Cu(1)−N(1)	82.9(3)
O(3)−Cu(1)−O(9)	96.5(2)
O(3)−Cu(1)−N(2)	82.8(2)
O(9)−Cu(1)−N(1)	95.9(2)
O(9)−Cu(1)−N(2)	102.3(3)
N(1)−Cu(1)−N(2)	96.3(3)
O(2)−C(8)−C(7)	117.2(8)
O(2)−C(8)−C(9)	118.5(8)
C(7)−C(8)−C(9)	124.3(7)

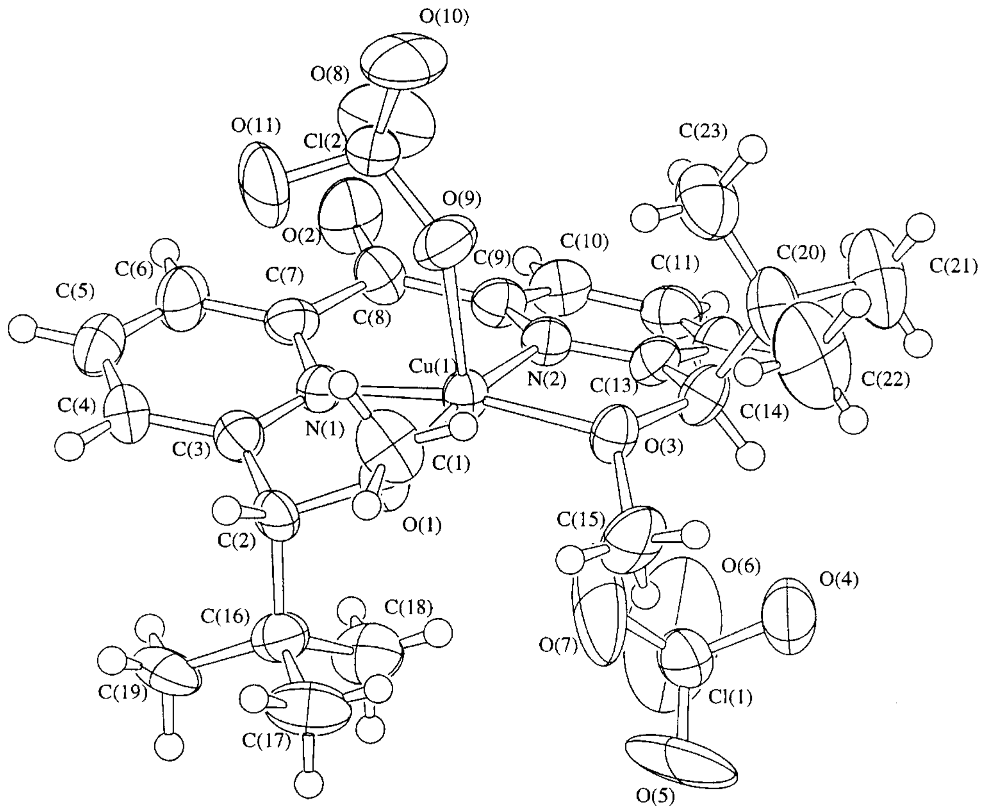
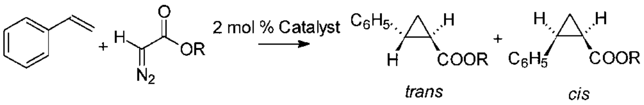


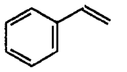
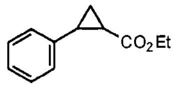
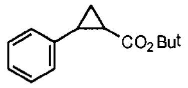
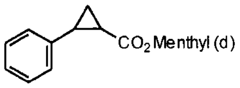
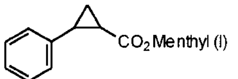
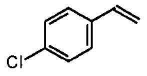
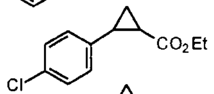
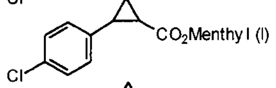
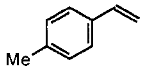
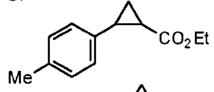
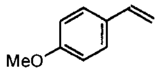
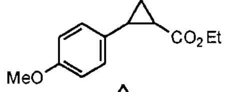
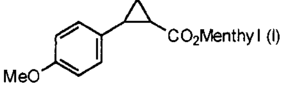
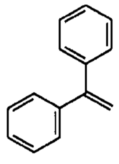
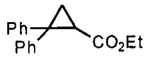
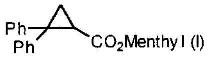
Figure 1. Molecular structure of complex **7**

The use of copper complexes prepared from CuOTf and bipyridines as catalysts in the cyclopropanation of alkenes have been reported by Katsuki et al. and our group.[9] To investigate if these dipyridyl ketone ligands had similar reactivity, we studied the cyclopropanation with complex **7** (Scheme 3). The perchlorate complex **7** was found to be an active catalyst in cyclopropanation with ethyl diazoacetate (EDA). A high *trans*/*cis* ratio (79:21) was obtained, but the complex showed very poor enantioselectivity (3% for both *trans* and *cis* isomers). On the other hand, the triflate complexes, which were prepared by reacting **4a–d** with copper(II) triflate, served as more selective catalysts. The results for asymmetric cyclopropanation of styrenes with different ligands are shown in Table 2. The reactions were carried out in the presence of 2 mol-% copper catalyst, 2.2 mol-% chiral ligand, 0.5 M alkyl diazoacetate and excess styrene (2.0 M). In all cases, the yields of the isolated cyclopropanes were excellent, but the enantioselectivities obtained were moderate. With EDA, the C_2-symmetric ligand **4a**, which contains the bulky *tert*-butyl group, gave the highest *ee* for both *trans* (50% *ee*) and *cis* (44% *ee*) isomers, whereas the C_2-symmetric ligand **4b** and the C_1-symmetric ligands **4c** and **4d** showed poor enantioselectivity. Compound **4a** was found to be the best ligand, although other styrene substrates were also tested. In all cases, the chemical yields of the cyclopropane ester were good. For substituted styrenes, the *trans*/*cis* ratios were about 60:40 (Table 2, entries 1, 8, 10 and 11) and the enantioselectivities were between 50 and 59% *ee* for the *trans* isomers and between 38 and 45% *ee* for the *cis* isomers. There is no strong dependence on en-



Scheme 3. Cyclopropanation of styrene

Table 2. Catalytic asymmetric cyclopropanation with chiral copper(II) dipyridyl ketone complexes

entry	ligand	substrate	product	*trans* : *cis*	% *ee*, *trans*	% *ee*, *cis*	yield %
1	**4a**			60 : 40	50 (1R,2R)	44 (1R,2S)	83
2	**4b**			60 : 40	21 (1S,2S)	21 (1S,2R)	95
3	**4c**			68 : 32	1 (1S,2S)	14 (1S,2R)	85
4	**4d**			62 : 38	10 (1R,2R)	28 (1R,2S)	68
5	**4a**			65 : 35	47 (1R,2R)	30 (1R,2S) ee	80
6	**4a**			64 : 36	34 (1R,2R)	26 (1R,2S)	76
7	**4a**			73 : 27	60 (1R,2R)	58 (1R,2S)	83
8	**4a**			61 : 39	54 (1R,2R)	38 (N.D.)[a]	92
9	**4a**			83 : 17	57 (1R,2R)	31 (N.D.)[a]	80
10	**4a**			61 : 39	59 (N.D)[a]	43 (N.D.)[a]	83
11	**4a**			61 : 39	56 (1R,2R)	45 (N.D.)[a]	88
12	**4a**			85 : 15	56 (1R,2R)	28 (N.D.)[a]	91
13	**4a**			–	49 (1R)		79
14	**4a**			–	61 (1R)		77

[a] Not determined.

antioselectivity and *trans*/*cis* selectivity with both electron-donating and withdrawing groups. A 49% *ee* was observed for 1,1-diphenylethene (entry 13).

The effect of the diazo ester structure on *trans*/*cis* diastereoselectivity and enantioselectivity was evaluated with *tert*-butyl-, L-menthyl- and D-menthyl diazoacetate. As can be seen from entries 1, 5, 6 and 7 in Table 2, the *trans*/*cis* ratios for styrene increase when the R group changes from an ethyl to a bulkier group. L-Menthyl shows the greatest improvement. This is consistent with the trend previously observed with other copper catalysts. However, the enantioselectivities for *trans* and *cis* isomers only show an improvement for the L-menthyl group (entry 7). Even higher *trans*/*cis* ratios are observed with chlorostyrene and methoxystyrene (entries 9 and 12). The enantioselectivities for chlorostyrene (entry 9), methoxystyrene (entry 12) and 1,1-diphenylethene (entry 14) all show an improvement with the use of L-menthyl diazoacetate. When the ligands **4a** and **4d** were used with copper (II) triflate, the absolute configurations of the cyclopropane ester products formed from styrene were determined to be (1*R*,2*R*) and (1*R*,2*S*) for the *trans* and *cis* isomers, respectively, while **4b** and **4c** induce the formation of the (1*S*,2*S*) and (1*S*,2*R*) enantiomers. It is interesting to note that although **4a** and **4c** were both synthesized from **5**, the C_2 ligand **4a** gives 1*R* products whereas the C_1 ligand **4c** leads to 1*S* products. A similar observation was also observed with **4b** and **4d**.

In order to know more about the active intermediate in the reaction, the relative rates of cyclopropanation for substituted styrenes using ligand **4a** with EDA were determined through competition experiments. The Hammett plot of $\log(k_X/k_H)$ versus $\sigma(+)$ is shown in Figure 2, and a good $\sigma(+)\rho$ correlation was obtained with $\rho = -0.74$. Although the ρ value is similar to that reported by Kodadek and Woo et al. (−0.85) and Pérez et al. (−0.68) for the cyclopropanation of substituted styrenes using an EDA/iron(II) phophyrin system[15] and EDA/copper(I) tris(pyrazolyl)borate,[16] respectively, correlations to σ instead of σ(+) were found in the two latter systems. Nonetheless, the negative value for ρ supports the formation of an electrophilic metal−carbene complex intermediate and only a moderate positive-charge build-up at the benzylic carbon in the transition state. Although the mechanism is still elusive, it is believed that the metal carbene formed by the reaction between the Cu^I complex and the diazo compound is the active species. Based on the absolute configuration of the products obtained from the reaction with ligand **4a**, the sense of asymmetric induction observed here can be explained by the model shown in Scheme 4. This model is in agreement with that previously cited by Pfaltz for other *N*,*N*-bidentate ligands.[4a] In this model, ligand **4a** acts as a bidentate ligand and the metal carbenoid attacks the olefinic double bond according to pathway *a* and *b*. In case *a*, a repulsive steric interaction builds up between the ester group and the adjacent bulky *tert*-butyl group of the ligand. Therefore, pathway *b* is expected to be favored over pathway *a*. In case *b*, this will lead to the *cis*-(1*R*)- or *trans*-(1*R*)-cyclopropane esters, consistent with the experimental results.

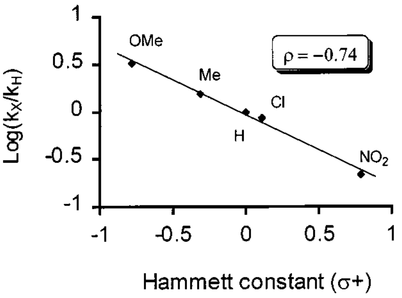
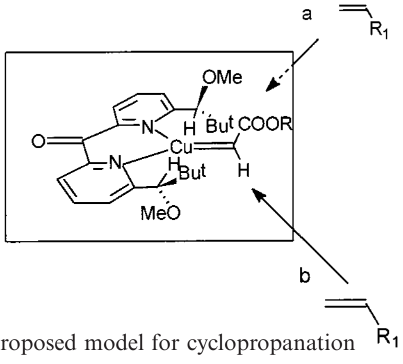


Figure 2. Hammett plot for the cyclopropanation of styrene with EDA using $Cu(OTf)_2$ and ligand **4a** as the catalyst



Scheme 4. Proposed model for cyclopropanation

Conclusion

In summary, we have successfully synthesized a novel chiral di-2-pyridyl ketone from the organometallic addition of a chiral pyridine derivative. The copper complexes of these ligands are active catalysts for cyclopropanation and *ee*s of up to 61% were observed. Comparison of the reactivity and enantioselectivity of ligand **4a** with other copper-catalyzed cyclopropanation reactions indicates that the active intermediates in these reactions are similar. We are continuing our efforts to study the use of these ligands in other catalytic asymmetric reactions.

Experimental Section

General Remarks: Toluene was distilled under N_2 from sodium. Dichloromethane and acetonitrile were distilled over calcium hydride. Diethyl ether and THF were distilled under N_2 over sodium/benzophenone. Chemicals were of reagent-grade quality and were obtained commercially. Infrared spectra were recorded in the range 500−4000 cm^{-1} as Nujol nulls or KBr plates on a Perkin−Elmer Model FTIR−1600 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz Mercury instrument. Positive ion FAB mass spectra were recorded as 3-nitrobenzyl alcohol matrices on a Finnagin MAT 95 spectrometer. Electron-ionization mass spectra were recorded on a Hewlett Packard 5890II GC instrument coupled with a 5970 mass-selective detector. Elemental analyses were performed on a Vario EL elemental analyser. Optical rotations were measured on a JASCO DIP−370 digital polarimeter.

Melting points were measured on an Electrothermal digital melting point apparatus.

General Procedure for the Synthesis of Ligands 4a and 4b: *n*-Butyllithium in hexane (2.5 M, 1.0 mL, 2.5 mmol) was added slowly to a solution of chiral bromopyridine (2.4 mmol) in THF (5.0 mL) at −78 °C. The resulting mixture was stirred at this temperature for 2 h. Ethyl chloroformate (1.2 mmol) in THF (5.0 mL) was cooled to −78 °C and added slowly to the yellowish brown solution. The solution was allowed to stir for 1 h. Methanol (5.0 mL) was then added and the mixture was warmed to room temperature. Water (5.0 mL) and HCl (10%, 5.0 mL) were then added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product purified by column chromatography.

Ligand 4a: Following the above procedure with **5** and the usual workup, followed by chromatography with petroleum ether/EtOAc (7:1), gave **4a** (0.300 g, 65%). − $[\alpha]_D^{25} = +167.8$ (c = 0.5, CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 1687 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.92 (s, 18 H), 3.26 (s, 6 H), 4.06 (s, 2 H), 7.58 (d, J = 7.5 Hz, 2 H), 7.85 (t, J = 7.8 Hz, 2 H), 8.01 (d, J = 7.5 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 26.1, 35.6, 57.8, 92.2, 123.9, 124.2, 135.8, 152.7, 160.2, 192.5. − Positive ion FAB mass spectra: m/z = 385 [M^+ + H]. − $C_{23}H_{32}N_2O_3$ (384.52): calcd. C 71.84, H 8.39, N 7.29; found C 72.49, H 8.29, N 6.78.

Ligand 4b: Following the above procedure with **6** and the usual workup, followed by chromatography with petroleum ether/EtOAc (5:1), gave **4b** (0.234 g, 65%). − $[\alpha]_D^{25} = -78.5$ (c = 0.2, CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 1681 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.48 (d, J = 6.0 Hz, 6 H), 3.34 (s, 6 H), 4.50 (q, J = 6.3 Hz, 2 H), 7.64−7.70 (m, 2 H), 7.89−8.10 (m, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 22.1, 56.8, 80.4, 122.3, 123.9, 137.1, 153.2, 162.6, 192.5. − Positive ion FAB mass spectra: m/z = 301 [M^+ + H].

General Procedure for the Synthesis of Ligands 4c and 4d: *n*-Butyllithium in hexane (2.5 M, 1.0 mL, 2.5 mmol) was added slowly to a solution of chiral bromopyridine (1.2 mmol) in THF (5.0 mL) at −78 °C. The resulting mixture was stirred at this temperature for 2 h. Ethyl picolinate (1.2 mmol) in THF (5.0 mL) was cooled to −78 °C and added slowly to the yellowish brown solution and this mixture was then allowed to stir for 1 h. Methanol (5.0 mL) was then added and the mixture warmed to room temperature. Water (5.0 mL) and 10% HCl (5.0 mL) were then added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product purified by column chromatography.

Ligand 4c: Following the above procedure with **5** and the usual workup, followed by chromatography with petroleum ether/EtOAc (5:1), gave **4c** (0.106 g, 31%). − $[\alpha]_D^{25} = +34.4$ (c = 0.5, CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 1686 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.94 (s, 9 H), 3.23 (s, 3 H), 4.02 (s, 1 H), 7.46−7.52 (m, 1 H), 7.60 (d, J = 8.1 Hz, 1 H), 7.84−7.92 (m, 2 H), 7.99 (d, J = 7.2 Hz, 1 H), 8.11 (d, J = 8.1 Hz, 1 H), 8.72 (d, J = 4.5 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 26.1, 35.7, 57.7, 92.1, 123.4, 124.3, 125.2, 126.0, 136.1, 148.8, 152.7, 153.9, 160.1, 192.6. − Positive ion FAB mass spectra: m/z = 285 [M^+ + H].

Ligand 4d: Following the above procedure with **6** and the usual workup followed by chromatography with petroleum ether/EtOAc (1:1) gave **4d** (0.073 g, 25%). $[\alpha]_D^{25} = -78.4$ (c = 1.0, CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 1685 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.48 (d, J = 6.3 Hz, 3 H), 3.35 (s, 3 H), 4.52 (q, J = 6.0, 1 H), 7.44−7.56 (m, 1 H), 7.66 (d, J = 6.9 Hz, 1 H), 7.84−8.02 (m, 3 H), 8.13 (d, J = 7.2 Hz, 1 H), 8.68−8.82 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 22.1, 56.8, 80.3, 122.3, 123.9, 125.3, 126.2, 136.4, 137.1, 148.8, 153.0, 153.8, 162.9, 192.4. − Positive ion FAB mass spectra: m/z = 243 [M^+ + H].

Synthesis of Copper Complex 7: Complex **7** was synthesized by adding ligand **4a** (0.24 mmol) in methanol (5 mL) to a stirred solution of copper(II) perchlorate (0.1 mmol) in methanol (5.0 mL). The mixture was stirred overnight. The volume of the mixture was reduced to about 1 mL and ether was then added. The blue solid formed was collected (57 mg, 88% yield). − IR (KBr): $\tilde{\nu}$ = 1687 cm^{-1}. − $C_{23}H_{32}Cl_2CuN_2O_{11}$ (646.96): calcd. C 42.70, H 4.99, N 4.33; found C 43.08, H 4.78, N 3.93.

X-ray Crystallographic Study: Suitable crystals of complex **7** were grown by dissolving it in acetonitrile and allowing diethyl ether to diffuse into the solution. Diffraction data were obtained on a Rigaku AFC7R diffractometer at ambient temperature. Intensity data were corrected for Lorentz and polarization effects. Absorption corrections based on the χ-scan technique were also applied. The structure was solved by direct methods (SIR 92) and refined on F by least-squares analysis. The absolute structure of the molecule was determined by analysis of both configurations, including the anomalous scattering effect. Hydrogen atoms were placed in their ideal positions (C−H, 0.95 Å) and included in the structure factor calculations, but were not refined. All calculations were performed on a Silicon Graphics workstation using the TeXsan package. Crystal data and details of the measurements are collected in Table 3.

Table 3. Crystallographic data for **7**

Data	**7**
Formula	$C_{23}H_{32}Cl_2CuN_2O_{11}$
F_w	646.96
Crystal system	Monoclinic
Lattice type	Primitive
a/Å	10.177(5)
b/Å	8.662(4)
c/Å	15.841(5)
V/Å^3	1395.2(8)
Space group	$P2_1$(#4)
Z	2
μ(Mo-K_α)	10.34 cm^{-1}
Temperature	28.0°C
Reflections collected (unique)	2636
Obs. Reflections [$I > 1.5\sigma(I)$]	2119
No. of variables	351
$2\theta_{max}$ (deg)	50.0
R, R_w	0.048, 0.047

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140108. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Procedure for Copper-Catalyzed Cyclopropanations: To a two-necked round bottom flask were added $Cu(OTf)_2$ (7.2 mg, 0.02 mmol), CH_2Cl_2 (2.0 mL) and the ligand (0.022 mmol) under nitrogen. The solution was stirred at room temperature for 2 hours. The alkene (4.0 mmol) and diazoacetate (0.2 mmol) were then added and the mixture was warmed at an oil bath temperature of 40 °C for 0.5 h. A solution of diazoacetate (1.0 mmol) in CH_2Cl_2 (0.5 mL) was then added to the reaction mixture over a period of 4 hours using a syringe pump. After the addition of diazoacetate, the mixture was allowed to stir for 16 hours at room temperature. The mixture was then workedup by removing the solvent and purifying the crude product by column chromatography (hexane/EtOAc). All the cyclopropanes obtained are known compounds and were characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy, and GC−MS. The enantiomeric excesses of the cyclopropanes were determined by capillary GC with Chiraldex β−PH column (30m × 0.25 mm) (entry 5) and HPLC with Daicel Chiralcel OJ column (entries 1−4, 8, 10, 13). For the substrates in entries 6, 7, 9, 11, 12 and 14, the *ee* values were determined by a previously reported procedure.[4a,17] Diastereoselectivities (*cis*/*trans* ratio) were measured by GC with an Ultra 2-crosslinked 5% PhMesilcone (25m × 0.2 mm × 0.33μm) column. Assignments of absolute configuration were by comparison with the elution order of authentic samples prepared by a literature procedure.[17]

General Procedure for Competition Reactions: To a two-necked round bottom flask were added $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), CH_2Cl_2 (1.0 mL) and the ligand (0.011 mmol) under nitrogen. The solution was stirred at room temperature for 2 hours. Styrene (2.0 mmol), substituted styrene (2.0 mmol) and ethyl diazoacetate (0.1 mmol) were added and the mixture was warmed at an oil bath temperature of 40 °C for 0.5 h. A solution of diazoacetate (0.5 mmol) in CH_2Cl_2 (0.5 mL) was then added to the reaction mixture over a period of 4 hours using a syringe pump. After the addition of diazoacetate, the mixture was allowed to stir for 16 hours at room temperature. The ratios of the resulting cyclopropane esters were determined by GC.

Acknowledgments

Financial support for this research from the Hong Kong Research Grants Council and the City University of Hong Kong (grant no. 7/00039) is gratefully acknowledged.

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Received February 10, 2000
[I00052]